Macromolecules **2003,** *36,* 8353−8360

Highly Branched Polyphenylenes with 1,3,5-Triphenylbenzene Fragments via Cyclocondensation of Acetylaromatic Compounds and Ni^0-Catalyzed Dehalogenation: Synthesis and Light Emission

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Received May 27, 2003; Revised Manuscript Received August 21, 2003

ABSTRACT: Highly branched photoluminescent polyphenylenes (PP) containing 1,3,5-triphenylbenzene (TPB) fragments were prepared via combination of cyclocondensation of acetylaromatic compounds and Ni^0-catalyzed dehalogenation. To develop optimal conditions for cyclocondensation of acetylaromatic compounds, we studied a model reaction of 1,3,5-triphenylbenzene formation using different solvents and catalysts. The maximum 85% yield of TPB was achieved using H_2SO_4 as a catalyst in ethanol−toluene medium at 50 °C for 5 h. Cyclocondensation polymerization of 4,4′-diacetyl diphenyl ether or 4,4′-diacetylbenzene in the presence of equimolar amounts of acetophenone (in the optimal conditions with respect to the soluble polymer yield) did not produce photoluminescent PP due to various defects in the polymer chain. Defect-free PP with starlike fragments were synthesized using Ni^0-catalyzed polymerization of aromatic bromides obtained by modification of 1,3,5-tri(*p*-bromophenyl)benzene. The molecular weights of the polymers were 6700 and 8600 Da. The maximum photoluminescence in solution (quantum yield of 96%) was obtained for the highly branched polymer with starlike TPB fragments, bearing no Br or acetyl groups. The PP of this kind also show very bright fluorescence in the solid state under UV irradiation at 360 nm so they can be considered as promising materials for OLED applications.

Introduction

Polyphenylenes (PP) are π-conjugated polymers drawing a considerable interest from the mid-1960s as thermally stable materials.[1] Nowadays, polyphenylenes are again in the focus of attention because of their unusual electrical and optical properties such as electrical conductivity, optical nonlinearity, luminescence,[2,3] and therefore the possibility of using in organic light emitting diodes (OLEDs).[4,5] Wide band gaps allowing emission of blue light (400−450 nm) are typical for polyphenylenes. The development of effective long-lived blue emitters remains a significant challenge in the field of OLEDs that makes polyphenylenes the polymers of interest.[6,7] PP can be synthesized using different avenues.[8−15] The majority of recent works were focused on linear PP.[7,16,17] One of the successful methods to synthesize linear PP is Ni^0-catalyzed homopolymerization of aromatic dibromides or dichlorides.[14,18−26] This method leads to defect-free structures and seems to be promising for synthesis of polyphenylenes designed for optoelectronic devices.

Normally linear poly-*p*-phenylenes (PPP) are insoluble in organic solvents that strongly limits their potential application for OLED. A reasonable way to increase solubility is to insert side groups in linear macromolecules. PPP containing certain substituents in phenyl rings (for example, alkyl, aryl, alkoxy, or acyl groups) can be either soluble or insoluble depending on their structure.[7,20,27−30] At the same time, often the length (or structure) of the substituents is not sufficient to separate the macromolecules and to prevent a self-quenching of luminescence due to migration of excitation energy. The solution of this problem allowing synthesis of effective blue emitters can be found in synthesis of polymers with very branched fragments containing no other substituents than benzene rings.

The example was shown in our recent work,[31] where the presence of branched aromatic fragments (in this case, in poly(phenylenevinylenes)) provided high luminescence intensity and blue luminescence maximum shift (at about 350 nm). The aromatic starlike blocks are luminophores themselves so they determined emission of the polymer molecules. This shows that the incorporation of branched phenylene blocks in side chains of the macromolecules impart the luminescence to the polymers, if the branched phenylene structure is defect-free.

Synthesis of branched polyphenylenes containing 1,3,5-triphenyl-substituted benzene rings was described in early 1990s.[32−34] The synthesis was based on a AB_2-type monomer which, in turn, was synthesized from 1,3,5-tribromobenzene by substitution of one bromine group with MgX group by Grignard reaction[33] or with $B(OH)_2$ group by Suzuki reaction.[32−34] The polymers prepared by these methods had low molecular weight, and the majority of them were soluble in common solvents. However, neither their structure nor optical properties were reported in refs 32−34. One might speculate that these methods should result in the formation of a number of defects in polymers; the

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10.1021/ma0347114 CCC: $25.00

polymers might also contain a significant amount of terminal bromo groups, but these issues were not discussed.

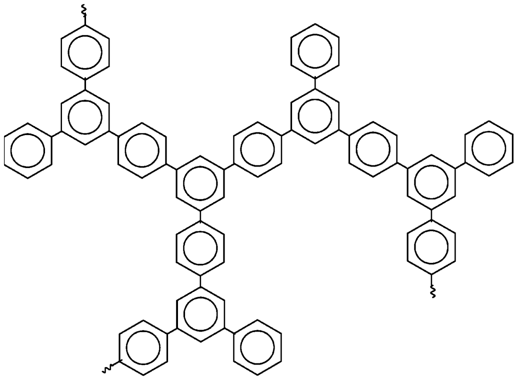
To synthesize branched polymers with solely phenylene rings in their structure, one can suggest the methods allowing generation of a new phenyl ring during polymer chain formation. The Diels−Alder reaction[11,13] is a method generating the hexaphenyl- and pentaphenylbenzene rings. A large family of well-defined macromolecules, consisting of several hexaphenylbenzenes, were described recently in refs 35−37. However, hexaphenylbenzene fragments are not luminescent.[31,38] Improvement comes from planarization of the phenyl rings, but the system becomes insoluble. To impart solubility to such a system, extra substituents are required, but this adds to the complexity of the synthesis.

Another polymer reaction resulting in the formation of 1,3,5- and 1,2,4-trisubstituted benzene rings is cyclotrimerization of aromatic ethynyl compounds reported in the 1970s and discussed in a review article.[39] Recent works[40−42] reported the development of this synthetic method and first showed the luminescent properties of the branched polyphenylenes prepared in this way. The emission efficiency was found to be from 15% to 46% in solution.

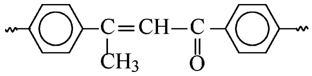
Some works, summarized in a review article,[10] described polyphenylene synthesis based on trimerization cyclocondensation of diacetylaromatic compounds and acetophenone in the presence of acidic catalysts to give exclusively 1,3,5-substituted triarylbenzenes.[43,44]

Since 1,3,5-triphenylbenzene (**1**, TPB) is an important “building block” of branched polyphenylenes, there were attempts to optimize the synthesis of **1** starting from the early work by Wirth et al.,[45] describing synthesis of 1,3,5-triphenylbenzene with no more than 50% yield by cyclocondensation of acetophenone in the presence of various acids. Further optimization of this reaction carried out with triethylformate as a ketalizing agent in benzene using gaseous HCl as a catalyst is described in refs 10 and 44. It allowed synthesis of **1** with about 75% yield. Use of tetrachlorosilane in dry ethanol, resulting in HCl and tetraethoxysilane (the latter is a ketalizing agent), led to formation of 1,3,5-triphenylbenzene with a comparable yield.[46]

Cyclotrimerization polycondensation of the equimolar amounts of diacetyl- and monoacetyl-containing benzenes results in the polymer where chain growth occurs due to interaction of three acetyl groups:[43]



This reaction has two drawbacks: (i) it may lead to the gel formation and should be stopped before gelation occurs (by precipitation in ethanol), and (ii) a polymer contains many defect fragments due to side reactions. The major side reactions are an incomplete cyclization, i.e., dimerization instead of cyclization with formation of β-methylchalcone groups



and formation of linear and cyclic vinylene-containing products and also pyrylium salts.[10] According to refs 44 and 47, this method leads to oligomers containing on average 7−8 TPB units and about two β-methylchalcone fragments. These oligomers are soluble in chloroform, benzene, dioxane, DMF, and other conventional solvents due to highly branched structure; however, they bear defect fragments and are characterized by high polydispersity ($M_w/M_n = 6.8-9.9$).

Thus, trimerization cyclocondensation developed in the 1970s leads to soluble branched polyphenylenes containing 1,3,5-triphenyl-substituted benzene rings and a number of defect fragments. The defect fragments were of no concern when thermal stability of a polymer was a target property, but this method could not be considered as a viable route for synthesis of polymers with light emitting properties.

The modern demands for OLEDs require a very robust synthetic procedure to obtain highly emissive PP with high yields. Since these PP should be both soluble in organic solvents and defect-free to provide high emission, we suggest here a combination of two techniques: (i) cyclocondensation of monoacetyl aromatic compounds with trimer formation (a central part of a starlike polymer)[31] and (ii) Ni^0-catalyzed dehalogenation for synthesis of branched defect-free polymers. In this paper we also report the modification of the cyclocondenation procedure, allowing us to obtain cyclotrimers with a high yield, and also structure and properties of branched PP with starlike fragments.

Experimental Section

General Data. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400. FTIR spectra were recorded on a Bruker IFS 48 instrument. Mass spectrometry was performed using AEIMS-30 and Kratos MS-890. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) at a flow rate of 1 mL/min $CHCl_3$ with injector Rheodyne, Milton-Roy UV detector, and PL-gel columns with 100, 500, and 5×10^3 Å pore sizes and with polystyrene standard. In some cases $\bar{M}_n$ was determined by the ebullioscopy method using the EP-68. Molecular weights were also determined from sedimentation data using ultracentrifuge MOM 3180 (Hungary) at $T = 25 \pm 0.1$ °C in THF or DMF.

Yields of **1** in model reactions have been determined by quantitative thin-layer chromatography.[48] Liquid chromatography was performed with a LC-31 Bruker, with UV detector ($\lambda = 254$ nm) at room temperature with the glass column Jesser, silica gel Separon SGX, and methanol as an eluent at 5 mL/min. UV/vis spectra were taken on a Hitachi 150-20 spectrometer. The emission spectra were obtained from solutions in $CHCl_3$ with a Jobin-Yvon 3CS spectrofluorimeter. Quantum yields were calculated according to ref 49 using quinine sulfate in 0.1 N sulfuric acid as a reference ($\phi_f = 0.55$). The optical path length was 1 cm. The absorbance of the samples and the references was kept below 0.2 (in $CHCl_3$) at the excitation wavelength.

Flash chromatography was performed with a silica gel 60, 230−400 mesh ASTM (Merck or Macherey-Nagel) column.

Materials. All reagents and chemicals were purchased from Aldrich Chemical Co. Acetophenone was distilled before use. Ethyl orthoformate was distilled over K_2CO_3. Benzene was

Table 1. The 1 Yield in the Acetophenone Cyclocondensation in Different Solvents at 20 °C

				yield of TPB in different solvents, %			
run	catalyst	catalyst amount, wt %	time, h	benzene	toluene	ethanol	ethanol:toluene = 1:1 (vol)
1	HCl (gas)	120[a]	1	62	40	60	65
2	HCl (gas)	120[a]	2	76	76	70	72
3	H_2SO_4, conc	20	96	13	28	5	12
4	$CH_3C_6H_4SO_3H$	15	96	25	15	5	10
5	$BF_3{\cdot}O(C_2H_5)_2$	30	96	27	57	6	49
6	CH_3SO_3H	20	96	71	70	63	70
7	CF_3SO_3H	20	96	72	69	70	71

[a] Here and in Table 2 concentration of HCl (gas) is in mL/min.

dried with P_2O_5 and then distilled over Na. Gaseous hydrogen chloride was prepared by dropwise addition of concentrated H_2SO_4 to NaCl. DMF was distilled over CaH_2 in dry argon. All other reagents and starting materials were used as received. 4,4′-Diacetyldiphenyl oxide was prepared by standard Friedel−Crafts acylation of diphenyl ether with acetyl chloride in the presence of anhydrous $AlCl_3$ in dichloroethane.[50] After recrystallization from ethanol, the product had mp of 101−102 °C.[50]

Synthetic Procedures. *Synthesis of 1,3,5-Tri(4-bromophenyl)benzene (**2**).* 1,3,5-Tri(4-bromophenyl)benzene was synthesized by cyclocondensation of *p*-bromoacetophenone (60 g, 0.3 mol) in the presence of 1.2 mol excess of ethyl orthoformate (65.1 mL, 0.36 mol) in dry benzene (100 mL), bubbling gaseous hydrogen chloride through the solution for 1 h at room temperature. When H_2SO_4 was used as a catalyst, 100 mL of ethanol−toluene mixture (1:1 vol) contained 20 g (11 mL) of concentrated H_2SO_4 and the same amount of ethyl orthoformate; the reaction was carried out at 50 °C for 5 h. The precipitate obtained after pouring reaction solution in ethanol was isolated, rinsed with acetone, and recrystallized from chloroform. In HCl/benzene medium the yield was 50%, and in H_2SO_4/ethanol−toluene, the yield reached 62%; mp = 267−268 °C (262 °C[51]). MS: m/z = 543 [M^+]. Elemental analysis data for $C_{24}H_{15}Br_3$: Calculated, %: C, 53.07; H, 2.78; Br, 44.14. Found, %: C, 53.48; H, 3.08; Br, 43.48.

Synthesis of p-Ethynylacetophenone. A Schlenk tube was charged with *p*-bromoacetophenone (4.529 g, 0.0228 mol) and purged with argon. The temperature was raised to 70 °C, and triethyamine (3 mL), $(Ph_3P)_2PdCl_2$ (0.05 g), Ph_3P (1.0 g), trimethylsilylacetylene (3.9 mL, 0.0273 mol), and CuI (0.01 g) were added in argon counterflow. The mixture was stirred at 70 °C for 4 h. The resulting solution was mixed with chloroform and washed with water. The organic solution was dried over $CaCl_2$ overnight, and then the solvent was evaporated. The resulting solid was charged with 20 mL of 50 wt % NaOH, 10 mL of ethanol, 2 mL of THF, and 0.01 g of dibenzo-18-crown-6. The mixture was stirred for 3 h at 50 °C. After that the reaction solution was mixed with water. The product was extracted with diethyl ether and purified with column chromatography (silica gel as adsorbent, a mixture hexane: chloroform = 2:1 as an eluent). Yield is 27%; mp = 66−68 °C (67−68.5 °C[52]). MS: m/z = 132. Elemental analysis data for $C_{10}H_8O$: Calculated, %: C, 83.30; H, 5.56. Found, %: C, 83.19; H, 5.60. FTIR: 1680 cm^{-1} for C═O, 2110 cm^{-1} for C≡C, and 3100 cm^{-1} for ≡C−H.

Synthesis of [1,3-Di(4-bromophenyl)-5-(4-phenylethynyl-4-phenylacetyl)]benzene (**3**). A Schlenk tube purged with argon was charged with 1,3,5-tri(*p*-bromophenyl)benzene (**2**) (5 g, 0.0092 mol), 4-ethynylacetophenone (1.15 g, 0.090 mol), triethylamine (2 mL), and DMF (3 mL) and then heated to 80 °C under stirring. After that a catalytic system consisting of $(Ph_3P)_2PdCl_2$ (0.05 g), Ph_3P (1.0 g), and CuI (0.001 g) was added. The reaction mixture was stirred at 70−80 °C for 8 h. After cooling, the resulting solution was poured into methanol and the precipitate was collected. The final compound was purified with column chromatography (silica gel as adsorbent, chloroform as eluent). The yield was about 20%; mp = 248−250 °C. MS: m/z = 606 [M^+]. Elemental analysis data for $C_{34}H_{22}Br_2$: Calculated, %: C, 67.35; H, 3.66; Br, 26.36. Found, %: C, 66.84; H, 3.55; Br, 27.57. FTIR: 1680 cm^{-1} for C═O and 2110 cm^{-1} for C≡C.

Polyphenylenes with Acetyl End Groups. In a typical experiment (synthesis of polyphenylene **I** from 4,4′-diacetyldiphenyl ether and acetophenone as monomers), equimolar amounts of 4,4′-diacetyldiphenyl ether (4.6 mL, 0.04 mol) and acetophenone (1.0 g, 0.04 mol) were mixed with 48.7 mL of ethyl orthoformate (1.2 mol per every acetyl group) and dry solvent (70%). The reaction mixture was stirred about 30 min (until the monomer dissolved) and charged with a calculated amount of an acidic catalyst at a reaction temperature (see Table 2). After reaction completion, the reaction mixture was poured into ethanol. The yellow precipitate was isolated, washed with ethanol, and dried in a vacuum desiccator at room temperature.

The polymer **II** based on *p*-diacetylbenzene, and acetophenone was synthesized in the same way.

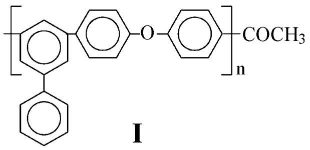
Synthesis of the Polyphenylenes by Ni^0-Catalyzed Reaction. Polymer **IV** was prepared by the method described elswhere.[53] Anhydrous $NiCl_2$ (2.6 mg, 0.02 mmol), Ph_3P (11.2 mg, 0.043 mmol), bipy (3.2 mg, 0.02 mmol), 4-bromobenzene (0.067 g, 0.425 mol), and 1,3,5-tri(4-bromophenyl)benzene (0.23 g, 0.425 mmol) were placed in a Schlenk tube purged with argon. The tube was evacuated and filled with argon five times. Then dry DMF (1 mL) was added by syringe purged with argon. The reaction mixture was quickly heated to 90 °C and then stirred at this temperature (for 6 h). In the first 10 min the reaction mixture became red-brown, which indicated the catalytic complex formation.[53] The resulting solution was poured into methanol; the precipitate was collected, washed with diluted HCl, water, and methanol, and dried in a vacuum desiccator at room temperature for 10 h. Yield was 52%. Elemental analysis data for $C_{30}H_{24}$: Calculated, %: C, 93.75; H, 6.25. Found, %: C, 92.52; H, 5.97; Br not found. Polymer **III** was prepared using the same procedure.

Results and Discussion

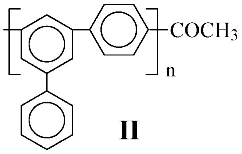
The first approach to synthesis of defect-free polyphenylenes with highly branched structure was to optimize formation of TPB fragments using cyclocondensation trimerization. The optimum conditions for synthesis of polyphenylenes using cyclocondensation of acetylaromartic compounds were thought to be benzene as a solvent and gaseous HCl as a catalyst.[10] However, when we carried out an optoelectronic study of the polyphenylenes obtained in these conditions, they showed no luminescence both in solutions and in a solid state. This was especially puzzling as model cyclotrimers with a 1,3,5-triphenyl-substituted benzene core, which are the main structural blocks of the polyphenylenes, showed luminescence with quantum yields in solutions in the range 29−72%.[31]

We suggested that these polyphenylenes show no luminescence because of its quenching by defect groups. We believe that the higher yield of 1,3,5-triphenylbenzene (**1**) in a model reaction of acetophenone cyclocondensation could determine the enhanced probability

Table 2. Characteristics of PP Synthesized in Different Reaction Conditions



I



II

run	polymer	catalyst	catalyst amount, wt %	solvent	T,°C	time, h	yield, %	mp, °C	η_{inh}, dL/g
1	I	HCl, gas	120	benzene	20	0.3	70	140−150	0.11
2	II					0.2	73	155−170	0.13
3	I	H_2SO_4, conc	5	ethanol			54	95−115	0.01
4			10				63	100−115	0.04
5			15				71	105−125	0.05
6			20		20	96	79	110−140	0.08
7			30				7 ins, 56 s[a]	110−145	0.06
8			50				25 ins, 38 s	130−180	0.02
9			20				73	165−175	0.14
10	II		20	ethanol/toluene			78	135−150	0.10
11	I		20		50	2	35	105−115	0.05
12	I	$CH_3-C_6H_4-SO_3H$	15				70	125−135	0.06
13			20	ethanol	20	96	68	120−140	0.05
14			30				51	120−155	0.05
15			15	ethanol/toluene			72	125−135	0.07
16			15		50	2	27	105−110	0.05
17	I	$BF_3{\cdot}O(C_2H_5)_2$	20		20	96	52	105−115	0.04
180			30	ethanol/toluene			66	110−135	0.05
19			30		50	2	76	110−145	0.14
20			40			96	66	115−140	0.07
21			50		30		65	115−145	0.08
22			30	ethanol		2	64	110−130	0.05
23	I	CH_3SO_3H	5				20	90−120	0.02
24			10		20	96	40	100−130	0.03
25			15	ethanol/toluene			62	110−130	0.06
26			20				76	135−150	0.07
27			20		50	2	60	93−135	0.06
28			30		20	96	40 ins, 20 s	135−160	0.02

[a] "s" stands for soluble fraction; "ins" stands for insoluble fraction; no notation means no insoluble polymer.

of the formation of the targeted fragments in the cyclocondensation polymerization of acetylaromatic compounds. On the basis of this, we studied cyclocondensation of acetophenone searching for reaction conditions leading to the higher **1** yield.

Model Cyclocondensation of Acetophenone. The cyclocondensation of acetophenone was carried out in polar and nonpolar solvents in the presence of different acidic catalysts. As acetophenone cyclocondensation proceeds through a carbocationic mechanism,[10,54] one might assume that this reaction should be inefficient in polar solvents since polar solvent should suppress the carbocation formation. Moreover, if the reaction medium is ethanol, additional complication is that ethanol is a reaction product so its abundance in the reaction solution should further suppress the reaction.

Nevertheless, a similar yield of **1** was obtained using not only benzene or toluene with HCl (76% in both cases) but also an ethanol/toluene mixture or pure ethanol as a solvent (70−72%). When sulfuric acid was used as a catalyst instead of HCl, the yields were close to about 70% and equal in benzene, toluene, and toluene/ethanol but slightly lower in ethanol (Table 1). Use of other acids listed in Table 1 leads to lower yields. To figure out the composition of the reaction products, the mixture obtained in ethanol/toluene as a solvent (Table 1, run 3) with low yield of **1** was studied by liquid chromatography. This composition allowed easier detection of byproducts because of their higher content. The product of acetophenone cyclocondensation was found to contain 10.6% **1**, 60.6% acetophenone, 26.7% mixture of β-methylchalcone and pyrylium salt, and 2.1% of other products of acetophenone condensation, probably analogous to those described in ref 10. This examination shows that comparatively low yields in the **1** syntheses can be mainly explained by (i) formation of byproducts of the condensation of acetophenone and triethyl orthoformate (pyrylium salts) and (ii) incomplete acetophenone condensation (β-methylchalcone formation).

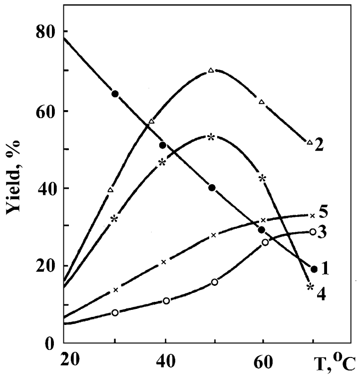


Figure 1. Temperature dependences of the **1** yield for different catalysts: HCl (1), H_2SO_4 (2), *p*-toluenesulfonic acid (3), $BF_3{\cdot}O(C_2H_5)_2$ (4), and CH_3SO_3H (5) in the toluene−ethanol mixture. Reaction time: 30 min.

The temperature dependence of the yield of **1** in toluene solution shows different behavior for different catalysts (Figure 1). For gaseous HCl, increase of reaction temperature resulted in decrease of the yield of **1**. This may occur because of a side reaction of HCl addition to intermediate vinyl ether and also because

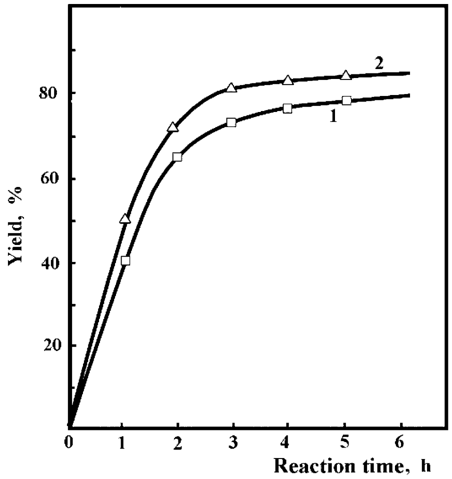
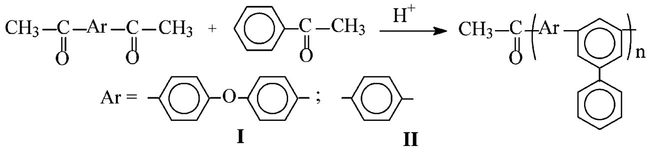


Figure 2. Dependences of the **1** yield on synthesis duration for H_2SO_4/ethanol (1) and H_2SO_4/ethanol−toluene (2). Reaction temperature: 50 °C.

Scheme 1



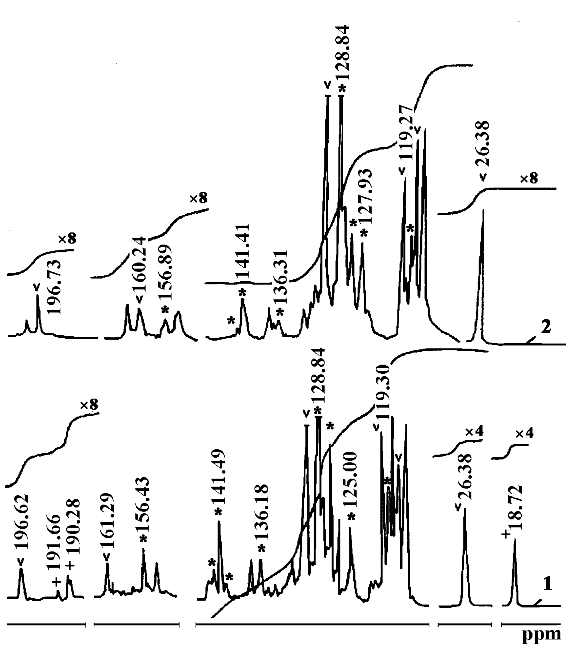


Figure 3. ^{13}C NMR spectra of polyphenylenes **I** synthesized in H_2SO_4/ethanol (1) and HCl/benzene (2) media: (*) fragments of **1** (1,3,5-triphenylbenzene); (+) β-methylchalcone fragments; notation ∨ is used to denote the diacetyldiphenyl ether end groups.

of HCl concentration decrease at higher temperatures. For *p*-toluenesulfonic acid and methanesulfonic acid, the yield increases with increase of the reaction temperature. Temperature dependence of the yield goes through a maximum value when the reaction is carried out with boron trifluoride diethyl etherate and sulfuric acid. Apparently, it is caused by faster formation of byproducts at temperatures higher than 50 °C for these two catalysts.

The yield of **1** depends also on reaction time. The yield strongly increased during the first 2 h and reached 85% for 5 h as shown in Figure 2 for two reaction solutions: H_2SO_4 in ethanol and ethanol/toluene at 50 °C. This temperature was chosen as it allows the highest yield of **1** for H_2SO_4 as a catalyst (see Figure 1). This dependence can be explained by increase of acetophenone conversion becoming quantitative (100%) for 5−6 h. Thus, 85% yield of **1** can be obtained in rather mild conditions (without aggressive gaseous HCl), but this value is still far from quantitative. At the same time, increase of the yield of **1** inspired us to try cyclocondensation for polymer synthesis considering that the synthetic procedure might be further optimized during polymerization. Since, in the case of polymers, all "byproducts" are fixed in the polymer structure as defect fragments, it should strongly influence the PP properties.

Cyclocondensation Polymerization of 4,4′-Diacetyl Diphenyl Ether and Acetophenone. Although for cyclocondensation polymerization with difunctional monomers we used the general conditions found for the synthesis of **1**, we had also to take into account that in polymer synthesis the reaction duration and temperature are restricted by possible and undesirable gel formation. Thus, conditions should be modified accordingly to give the highest yield of the soluble polymer in mild conditions and for the shortest time. We studied cyclocondensation polymerization of 4,4′-diacetyl diphenyl ether (DADPE) or 4,4′-diacetylbenzene (DAB) (see Scheme 1) in the presence of equimolecular amount of acetophenone with triethylformate[10,44] in the mixture ethanol:toluene = 1:1 (vol) in the presence of different acidic catalysts (Table 2).

The conditions presented in Table 2 show that yields higher than 70% for soluble polymers were obtained in the conditions similar to ones found for **1** (Table 1). For $BF_3 \cdot O(C_2H_5)_2$, the reaction temperature was increased to 50 °C, which led to shorter duration of the synthesis before gelation. As follows from the data presented in Table 2, the highest yield of soluble polymer (79%) was obtained with sulfuric acid at 20 °C for 96 h. It should be noted that the best yield of **1** (85%, Figure 2) was obtained in the same conditions, but at higher temperature (50 °C). For polymer synthesis, this temperature resulted in fast gelation and was not used.

The structure of the polymers **I** based on DADPE was studied using ^{13}C NMR spectroscopy. A signal assignment was performed in accordance with ref 44. The ^{13}C NMR spectra (Figure 3) of two polymer **I** samples obtained in runs 1 and 6 (Table 2) show a similar set of signals assigned to aromatic carbons. In addition, the ^{13}C NMR spectrum of the polymer **I** obtained in run 6 contains the signals at 18.58 ppm and at 190.20 ppm characteristic of methyl and carbonyl groups of β-methylchalcone defect fragments,[44] while in the ^{13}C NMR spectrum of the product from run 1, these signals are absent.

At the same time, the FTIR spectra of the polymer **I** samples from runs 1 and 6 show a weak band at 1660 cm^{-1}, which is characteristic of a carbonyl group of a β-methylchalcone fragment. Moreover, the spectrum of the sample from run 6 contains an additional band at 1720 cm^{-1} characteristic of ester group appearing as a result of β-methylchalcone group hydrolysis. Thus, judging by FTIR and ^{13}C NMR spectra, both polymer **I** samples contain defect fragments, but the polymer from run 6 shows an enhanced amount of these fragments compared to the polymer from run 1.

Scheme 2

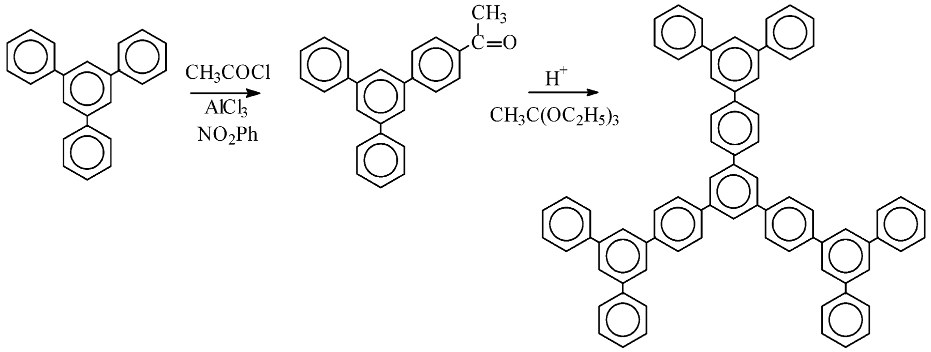


Table 3. GPC Data of Polyphenylenes I from Runs 1, 6, and 21 from Table 2

run from Table 2	catalyst	M_n	M_w	M_w/M_n
1	HCl	2560	5850	2.3
6	H_2SO_4	2020	6480	3.2
21	$BF_3{\cdot}O(C_2H_5)_2$	1430	2620	1.8

Three polymer **I** samples prepared with different catalysts (runs 1, 6, and 21, Table 2) were examined by GPC (Table 3). Comparison of the GPC data with the relatively low values of inherent viscosity (especially for polymers from runs 6 and 21) shows high branching in the polymers **I**.[55]

The polyphenylenes **II** based on DAB and acetophenone, i.e., the polyphenylenes consisting of solely phenylene groups, were synthesized in two systems: in benzene with HCl and in ethanol/toluene mixture with H_2SO_4 (Table 2, runs 2 and 10). The polymer from run 2 prepared with HCl has the higher molecular weight than the one from run 10 as follows from values of inherent viscosity and melting temperatures. Besides, the latter polymer (from run 10) bears the higher amount of defect fragments judging by the FTIR spectra (presence of the band at 1660 cm^{-1}). Unlike the polymers based on DADPE (**I**), where NMR signals are well resolved, for the polymers **II**, ^{13}C NMR spectra are not useful for their characterization as the NMR signals mainly overlap.

Thus, analysis of soluble branched PP obtained by cyclocondensation polymerization showed that they always contain some defect fragments and do not show photoluminescence. Synthesis of branched defect-free oligophenylene with 13 phenyl ring (tridecaphenyl or 1,3,5-tri[1,3-diphenyl(phenyl-5-yl)phenyl-4′-yl]benzene) was described by us earlier[31] using cyclocondensation of [1-(4′-acetylphenyl)-3,5-diphenyl]benzene (see Scheme 2). This molecule presents a second generation of PP dendrimer with **1** as a dendrimer center.

Here all byproducts were eliminated by purification after synthesis, and the final product showed intense photoluminescence in solution (quantum yield = 72%) at wavelength of about 370 nm (Figure 4). We believe that the higher generations of such dendrimers might result in enhancement of photoluminescence properties. However, as always with dendrimers of a higher generation, the synthesis is usually laborious and time-consuming. Another possibility is to lengthen the arms of the dendrimer center (obtained by cyclocondensation of acetylaromatic compounds) using some polymerization technique (for example, Ni^0-catalyzed dehalogenation) providing defect-free structure. This approach (described in the next section) should result in the branched polymers containing starlike fragments.

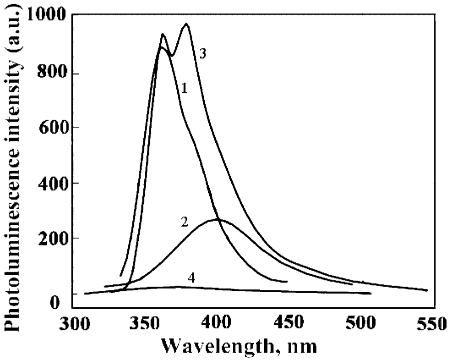


Figure 4. Photoluminescence spectra of tridecaphenyl (1), polyphenylene **III** (2), polyphenylene **IV** (3), and 1,3,5-tri(4-bromophenyl)benzene (4).

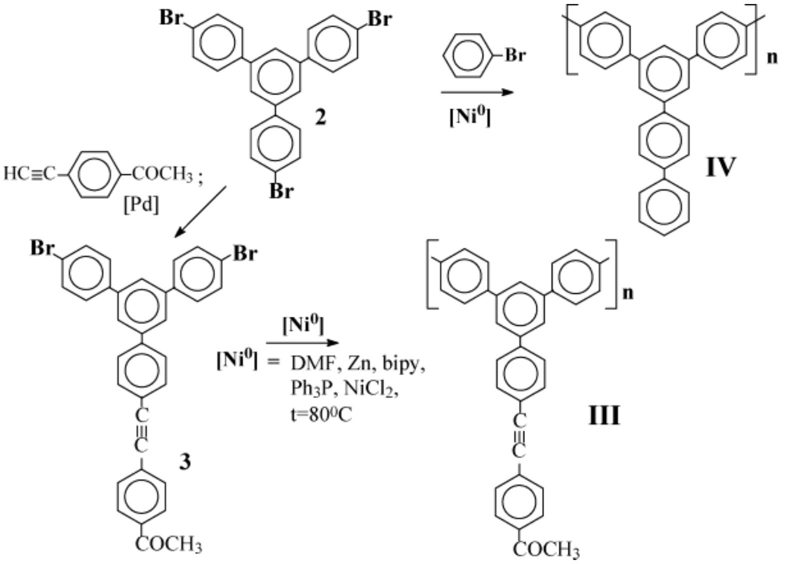
Ni^0-Catalyzed Synthesis of Highly Branched PP with Starlike Fragments. As discussed above and reported in refs 18, 26, and 53, dehalogenation of dibromo- or dichloroaromatic compounds catalyzed by Ni^0 complexes leads to defect-free PP structures. For synthesis of defect-free branched PP with TPB starlike fragments, we first synthesized the corresponding bromides and then used them as monomers in Ni^0-catalyzed polymerization.

New bromide was prepared starting from 1,3,5-tri(*p*-bromophenyl)benzene[51] (**2**) synthesized by cyclocondensation of *p*-bromoacetophenone. The synthetic procedure was based on the conditions developed for the synthesis of **1**.To prevent 3D cross-linking in Ni^0-catalyzed reaction with tribromide, we needed either to use some monobromide (to decrease the overall functionality of the system) or to convert tribromide to dibromide (to substitute one bromo group (out of three) in **2** for the other group (see Scheme III). However, reaction with equimolar amounts of phenylboronic acid and **2** resulted in nonselective substitution: by TLC the reaction product contained a mixture of mono- and disubstituted products along with remaining **2**. Our attempts to separate these products from each other using flash chromatography were unsuccessful.

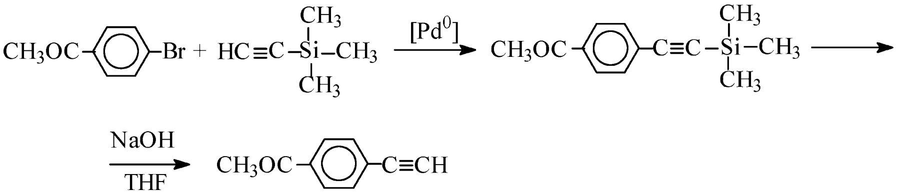
To obtain a monomer with two bromo groups, **2** was treated with 4-ethynylacetophenone, prepared by Scheme IV. In this case, the reaction also resulted in a mixture of products with different functionality, but because of the presence of polar $COCH_3$ groups, all products were easily separated from each other using column chromatography with chloroform:hexane = 1:2 (vol) mixture as an eluent. Compound **4** was obtained with 20% yield. Its purity was confirmed by mass spectrometry, elemental analysis, and FTIR.

Polymer **III** was prepared by Ni^0-catalyzed polymerization from **3** in DMF in the presence of anhydrous

Scheme 3



Scheme 4



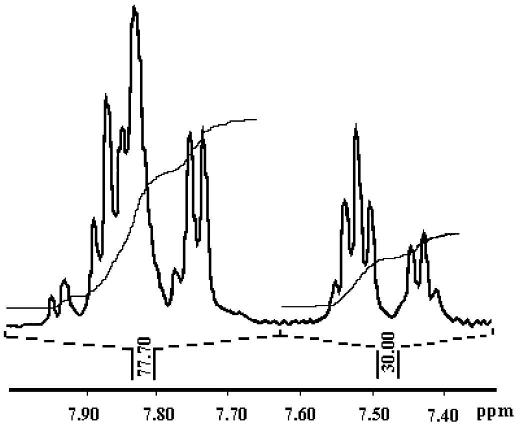


Figure 5. ^{1}H NMR spectrum of polyphenylene **IV** showing the signals area of aromatic protons.

NiCl$_2$, Zn, Ph$_3$P, and bipy in high-purity argon at 80 °C. Compound **2** containing three terminal bromine atoms was also used for direct polymer synthesis (polymer **IV**), but in this case, the equimolar amount of bromobenzene was added to prevent gelation.

The structure of polymers **III** and **IV** was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of the polymer **IV** (Figure 5) contains the signals at 7.37−7.56 ppm, which are characteristic for the protons of monosubstituted aromatic rings, and the signals at 7.70−7.95 ppm, which can be assigned to the remaining aromatic protons. In the ^{13}C NMR spectrum of the polymer **III**, the signal at 29.75 ppm is characteristic of methyl protons of the acetyl groups.

Molecular weights of polymers **III** and **IV** were examined by sedimentation in an ultracentrifuge. This method allows obtaining accurate values of weight-average molecular weight without using relative standards.[56] As polymer **III** cannot form additional branches (monomer **3** is strictly difunctional), the value of molecular weight allows calculating the number of repeating units. Since molecular weight of a repeating unit is 446, polymer **III** contains 15 repeating units. For polymer **IV**, this value cannot be calculated as the branching is terminated by addition of bromobenzene. However, if one assumes that a repeating unit in polymer **IV** is a disubstituted phenyl ring, this polymer contains 113 phenyl rings. Compared to tridecaphenyl, polymer **IV** contains more phenyl rings by a factor of 9; yet, the branched structure with prevailing TPB fragments is preserved.

Table 4. Characteristics of Polymers Prepared by Ni^0-Catalyzed Polymerization

polymer	mp, °C	$\bar{M}_w$, Da	PL QY, %
III	210−216	6700	17
IV	101−110	8600	96

The photoluminescence (PL) data for the polymers **III** and **IV** are shown in Table 4 and Figure 4. Unlike **1**, its brominated analogue **2** shows nearly no photoluminescence. The photoluminescence spectra of polymers **III** and **IV** and tridecaphenyl in chloroform solutions show blue emission, which is typical for completely aromatic structures.[6,15] Tridecaphenyl containing 13 benzene rings and 1,3,5-triphenyl-substituted benzene exhibits an intense photoluminescence peak at 360 nm with a PL quantum yield (QY) of 72%.[31] The spectra of the polymers differ depending on the polymer structure. The spectrum of polymer **IV** shows peaks at 360 and 380 nm (Figure 4); the position of the former fully coincides with the position of the tridecaphenyl peak. This polymer is characterized by a remarkably high PL QY (96%, Table 4). Since polymer **IV** is highly branched and resembles the tridecaphenyl structure, the similarities in their photoluminescence properties might be expected.

For polymer **III**, emission is less intense with PL QY (17%) and has a strong red shift: the fluorescence spectrum of polymer **III** peaked at about 400 nm. We think that quenching of luminescence might occur due to the presence of acetyl end groups enhancing interaction between neighboring chains, while the red shift should be caused by the difference in the structure: less branching and lack of starlike fragments. The important property of these PP is very bright fluorescence in the solid state under UV irradiation at 360 nm, so these polymers can be considered as promising materials for OLED applications.

Conclusions

The results reported here show that highly branched photoluminescent PP bearing TPB fragments can be prepared using cyclocondensation of acetylaromatic compounds for synthesis of TPB units and Ni^0-catalyzed dehalogenation for polymer chain propagation.

The model study of TPB synthesis by varying reaction conditions and types of catalysts and solvents showed that the highest TPB yield of 85% can be achieved in the H_2SO_4/ethanol−toluene medium, but no conditions were found to achieve a quantitative TPB yield. Further optimization of cyclocondensation conditions with respect to polymerization of acetylaromatic compounds allowed us to synthesize soluble PP with comparatively high yields (up to 79%) but with a number of defect fragments (for example, β-methylchalkone groups) in the polymer chains resulting in no photoluminescence.

When initial starlike fragment (1,3,5-triphenyl-substituted benzene ring) was obtained by cyclocondensation (in optimal conditions), while further polymerization was carried out using Ni^0-catalyzed polymerization, this resulted in defect-free polymers showing very intense photoluminescence in chloroform solutions (up to QY 96%). This value exceeds the one of tridecaphenyl (QY 72%). These PP show also very bright fluorescence in the solid state under UV irradiation.

Acknowledgment. Financial support for this work was provided by Russian Foundation for Basic Research (Grants 01-03-32937 and 02-03-32613).

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MA0347114